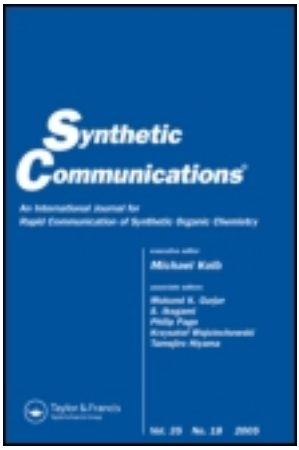

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DICYCLOHEXYLBORANE-CATALYZED HYDROBORATION OF 1-HALO-1-ALKYNES WITH 9-BORABICYCLO[3.3.1]NONANE

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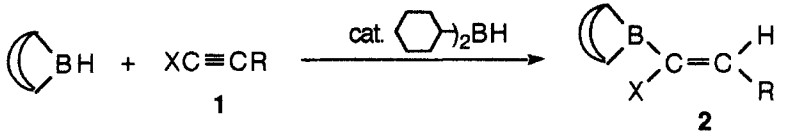
Abstract: A catalytic amount of dicyclohexylborane accelerates the hydroboration of 1-halo-1-alkyne (**1**) with 9-BBN to provide *B*-[(*Z*)-1-halo-1-alkenyl]-9-BBN (**2**) regio- and stereo-selectively.

In the course of our studies on the synthesis of functionally substituted organoboranes,[1] we were interested in *B*-[(*Z*)-1-halo-1-alkenyl]-9-BBN (**2**) prepared by the hydroboration of 1-halo-1-alkyne (**1**) with 9-borabicyclo[3.3.1]nonane (9-BBN), because 1-halo-1-alkenylboranes were versatile intermediates for organic synthesis.[2] However, the hydroboration of **1** with 9-BBN, the most simple method for the preparation of **2**, is sluggish under usual hydroboration conditions,[3,4] and thus it can not be used practically. For example, the hydroboration of 1-bromo-1-hexyne (**1b**) with 9-BBN in tetrahydrofuran (THF) requires 30 h to complete the reaction at room temperature,[4] while the hydroboration with dialkylborane, such as dicyclohexylborane[5] and 1,1,2-trimethylpropylcyclohexylborane,[6] proceeds smoothly even at 0 °C and below 0 °C. Accordingly, it is desirable to establish a methodology for

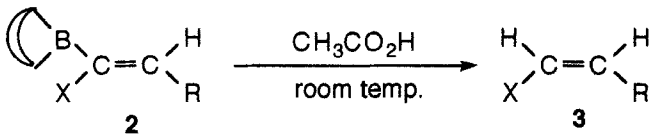
acceleration of the hydroboration. We wish to report here a dicyclohexylborane-



Scheme 1

catalyzed hydroboration of **1** with 9-BBN where the reaction is completed in a very short reaction time, providing **2** almost quantitatively (Scheme 1). To the best of our knowledge, this is the first time that hydroboration with 9-BBN is promoted by catalysis.

The experimental results of the hydroboration of selected **1** are shown in Table 1. The acceleration of the hydroboration by the use of a catalytic amount of dicyclohexylborane was remarkable. For example, in the presence of 5 mol% of dicyclohexylborane in THF the reaction of 1-chloro-1-hexyne (**1a**) with an equiv. of 9-BBN was completed in 4 h at room temperature, whereas in the absence of dicyclohexylborane a similar reaction required about 50 h for completion at room temperature.[4] The ^{1}H NMR spectrum of the reaction product, obtained after removal of the solvent, showed the presence of an alkenyl triplet (δ 6.82, *J* 6.8 Hz). On the other hand, the reaction mixture was protonolyzed with acetic acid[5] (Scheme 2) to afford (*Z*)-1-chloro-1-hexene (**3a**) stereoselectively in 98% yield. These results indicate that the hydroboration occurs regio- and stereo-selectively



Scheme 2

Table 1 Dicyclohexylborane-catalyzed hydroboration of 1-halo-1-alkynes with 9-BBN and protonolysis with acetic acid [a]

	1		Reaction	2		3	
	X	R	conditions [b]	Alkenyl proton δ [c]		Yield (%) [d]	
1a	Cl	*n*-C_4H_9	r. t., 4 h	(**2a**)	6.82	(**3a**)	98
1b	Br		r. t., 1 h	(**2b**)	7.07	(**3b**)	99
			0 ℃, 4 h			(**3b**)	95
1c	I		r. t., <1 h	(**2c**)	6.90	(**3c**)	99
			0 ℃, 6 h			(**3c**)	86
1d	Br	Ph	r. t., 6 h	(**2d**)	7.68	(**3d**)	92 (85)
1e	I		r. t., 2 h	(**2e**)	7.76	(**3e**)	83
1f	Br	-$(CH_2)_3Cl$	r. t., 1 h	(**2f**)	6.88	(**3f**)	99 (94)
1g	Br	-CH_2OCH_3	r. t., 2 h	(**2g**)	6.93 [e]	(**3g**)	96

a) The reaction of 1-halo-1-alkyne (1 mmol) with 9-BBN (1 mmol) in THF was carried out in the presence of dicyclohexylborane (0.05 mmol).

b) r. t. = room temp.

c) ^{1}H NMR spectra of the hydroboration product, after removal of THF, were obtained in $CDCl_3$ solutions cotaining TMS. Isomeric purity was 97~99 %, except for **2g**.

d) Determined by GLC and based on amount of 1-halo-1-alkyne used. Isolated yields are given in parentheses.

e) The **2g** : **2g'** regioisomer ratio, determined by the ^{1}H NMR spectrum, was 87 : 13. The alkenyl proton of **2g'** appeared as a broad triplet at δ 7.31.

(*cis*-addition manner) to provide quantitatively *B*-[(*Z*)-1-chloro-1-hexenyl]-9-BBN (**2a**), a monohydroboration product.

Similar hydroborations of 1-bromo-1-hexyne (**1b**) and 1-iodo-1-hexyne (**1c**) proceeded more rapidly than that of **1a**. Thus, the reactions of **1b** and **1c** were completed in 1 h and within 1 h to provide *B*-[(*Z*)-1-bromo-1-hexenyl]-9-BBN (**2b**) and *B*-[(*Z*)-1-iodo-1-hexenyl]-9-BBN (**2c**) in quantitative yields with high regio- and stereo-selectivities. These products were confirmed by ^{1}H NMR examination and protonolysis. It was also noted that the reaction of **1b** or **1c** proceeded sufficiently even at 0 °C.

In similar reaction conditions 1-bromo-2-phenylethyne (**1d**), 1-iodo-2-phenylethyne (**1e**), 1-bromo-5-chloro-1-pentyne (**1f**) and 1-bromo-3-methoxy-1-propyne (**1g**) were hydroborated smoothly, and on protonolysis the corresponding (*Z*)-1-halo-1-alkenes, (*Z*)-1-bromo-2-phenylethene (**3d**), (*Z*)-1-iodo-2-phenylethene (**3e**), (*Z*)-1-bromo-5-chloro-1-pentene (**3f**) and (*Z*)-1-bromo-3-methoxy-1-propene (**3g**), were obtained in good yields with high stereoselectivities.

In addition, the ^{1}H NMR examinations of the hydroboration mixtures revealed that the boron atom was oriented to the terminal carbon atom regioselectively to provide **2** except for the case of **1g** where two regioisomers, *B*-[(*Z*)-1-bromo-3-methoxy-1-propenyl]-9-BBN (**2g**) and *B*-[(*Z*)-1-bromo-3-methoxy-2-propenyl]-9-BBN (**2g'**) were formed in a ratio of 87 : 13.

The reaction is speculated to proceed in the following way. Thus, in the first stage of the reaction more reactive dicyclohexylborane may hydroborate **1** to give (*Z*)-1-halo-1-alkenyldicyclohexylborane, and then the bulky dicyclohexylboryl group may be displaced by less bulky 9-borabicyclo[3.3.1]nonyl group to provide **2**. In order to explore the occurrence of such a displacement reaction, (*Z*)-1-bromo-1-hexenyldicyclohexylborane was reacted with an equiv. amount of 9-BBN

in similar conditions, and then the reaction mixture was oxidized at 0 °C by alkaline hydrogen peroxide. If *B*-[(*Z*)-1-bromo-1-hexenyl]-9-BBN (**2b**) is formed by the displacement reaction, treatment of **2b** with aq. NaOH must result in cyclooctyl transfer along with elimination of bromo anion and give 1-(5-hydroxy)cyclooctyl-1-hexanone on the following oxidation. Indeed, the sequence of reactions gave the above compound, indicating that the displacement reaction occurs. A similar displacement reaction has been also appeared in our previous work.[7]

Although a more detailed study is needed, the present catalytic reaction, which realises the monohydroboration efficiently and stereoselectively providing **2**, enables us to utilize **2** as a potential intermediate for organic synthesis.

Experimental

General procedure for the dicyclohexylborane-catalyzed hydroboration, followed by protonolysis with acetic acid. A THF solution of 9-BBN (0.49 mol dm^{-3}, 2.04 ml, 1 mmol) and a THF suspended solution of dicyclohexylborane (0.1 mol dm^{-3}, 0.5 ml, 0.05 mmol) were placed in a flask under an Ar atmosphere at 0 °C. 1-Halo-1-alkyne (1 mmol) was added to the stirred suspension, and the mixture was allowed to warm to room temperature. After completion of the reaction , the reaction mixture was cooled to 0 °C, and acetic acid (0.5 ml) was added to the mixture. The solution was stirred for overnight at room temperature, and then oxidized by alkaline hydrogen peroxide (3 mol dm^{-3} NaOH, 4 ml; 30% H_2O_2, 0.5 ml) at 0 °C. The mixture was extracted with diethyl ether, and the combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography using pentane or pentane–dichloromethane (95 : 5) as eluent.

(*Z*)-1-bromo-2-phenylethene (**3d**): IR (film)/cm^{-1} 3080, 3020, 2920, 1615, 1490, 1445, 1070, 1030, 770, 695 and 570; ^1H NMR (200 MHz, $CDCl_3$, TMS) δ

6.42 (1H, d, *J* 8.0 Hz), 7.06 (1H, d, *J* 8.0 Hz), 7.3–7.45 (3H, m) and 7.65–7.75 (2H, m); ^{13}C NMR (200 MHz, $CDCl_3$, TMS) δ 106.3 (=CH), 128.2 (2 × =CH), 128.3 (=CH), 128.9 (2 × =CH), 132.3 (=CH) and 134.9 (=C).

(*Z*)-1-bromo-3-methoxy-1-propene (**3g**): IR (film)/cm^{-1} 2925, 2820, 1625, 1450, 1375, 1290, 1205, 1180, 1105, 965 and 665; ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 3.36 (3H, s), 4.11 (2H, braod d, *J* 3.9 Hz) and 6.2–6.4 (2H, m); ^{13}C NMR (200 MHz, $CDCl_3$, TMS) δ 58.3 (Me), 70.3 (CH_2), 109.4 (=CH) and 132.0 (=CH).

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